J. Org. Chem., 47(18), 3486-3495 (1982)

Adducts of Anthrahydroquinone and Anthranol with Lignin Model Quinone Methides. 1. Synthesis and Characterization

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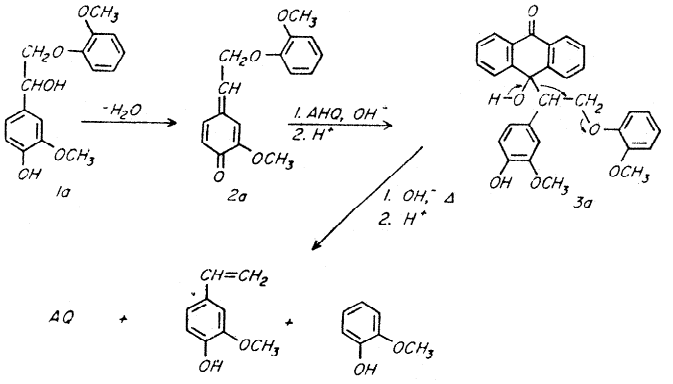
Adduct formation of anthrahydroquinone (9,10-dihydroxyanthracene, AHQ) or anthranol (9-hydroxyanthracene) with lignin model quinone methides (4-methylenecyclohexa-2,5-dienones) was established. This reaction is thought to be the key step in AHQ-catalyzed delignification of wood under alkaline pulping conditions. Numerous quinone methides derived from both 1-aryl-2-*O*-arylethyl and 1-aryl-2-*O*-arylpropyl lignin models were used. A typical example is the reaction of the quinone methide derived from 1-(3-methoxy-4-hydroxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol with AHQ to give the adduct *threo*-1-(3-methoxy-4-hydroxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propan-3-ol. ^{1}H NMR spectra of the adducts revealed large diamagnetic shifts of the protons in the 1-aryl substituent due to its close approach to the shielding regions of the anthracenyl moiety. This effect dimished with increasing size of the 10-substituent (H to OH to OAc). In AHQ adducts, intense hydrogen bonding between the 10-OH and the ether oxygen of the 2-aryl ether substituent was indicated by a large paramagnetic shift of the hydroxyl proton. The unusually large diamagnetic and paramagnetic shifts reflect a distinct rigidity of the adduct conformation that is more pronounced in the adducts containing a propyl side chain.

The significant rate increase in alkaline delignification of wood induced by catalytic quantities of anthraquinone (AQ) has generated worldwide interest in the pulp and paper industry.[1-5] In a model investigation of the catalysis mechanism utilizing **1a** as a lignin model (Scheme I), a

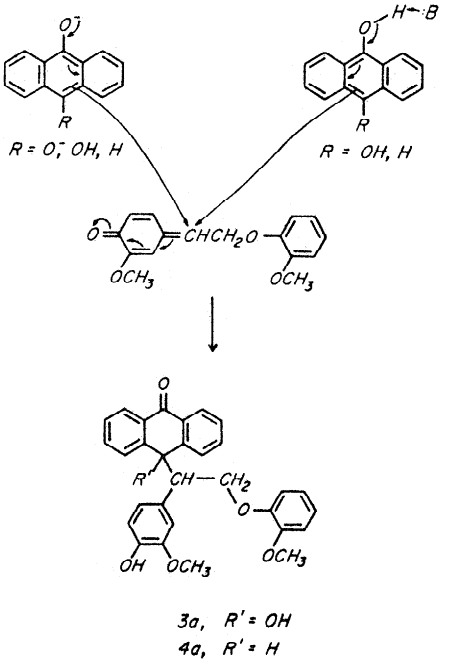
[†] Maintained at Madison, WI, in cooperation with the University of Wisconsin.

(1) H. H. Holton, U.S. Patent 4 012 280 (1977).
(2) K. L. Ghosh, V. Venkatesh, W. J. Chin, and J. S. Gratzl, *Tappi*, 60 (11), 127 (1977).

Scheme I



Scheme II



possible key intermediate was isolated.[6] The intermediate was characterized as the adduct **3a** formed via the quinone methide **2a**[7-9] and anthrahydroquinone (AHQ), the two-electron reduction product of AQ.[10] The structure of **3a** was subsequently confirmed.[11a] Also, the preparation of analogous AHQ and anthranol adducts with quinone methides derived from simple benzyl alcohols has recently been reported.[11b]

When **3a** is heated in aqueous alkali (>50 °C), it quantitatively decomposes into AQ, 4-vinylguaiacol, and guaiacol,[6] presumably by a heterolytic fragmentation[12] mechanism (Scheme I). The net result of the adduct formation and subsequent fragmentation is the cleavage of the β-aryl ether bond in **1a**. This bond accounts for a major portion of linkages in the lignin polymer, and its rate of cleavage in model systems has been correlated with the rate of delignification under various pulping conditions.[5,8,9,13] Moreover, in a reducing environment such as typical soda pulping conditions the liberated AQ is rapidly reduced to AHQ, and the cleavage of the β-aryl ether bonds becomes catalytic.[10]

The corresponding adducts with anthranol (anthracen-9-ol) are of interest because, like AHQ, anthranol (the alkali-stable tautomer of anthrone) is also a reduction product of AQ and forms to some extent under alkaline pulping conditions.[14] It has been shown that AHQ and anthranol react with quinone methides in an analogous fashion (Scheme II).[6] Although anthranol may play a role in the catalytic cleavage of β-ether bonds, the mechanisms are presently unknown. However, the alkaline degradation pathway of anthranol adducts cannot correspond to that proposed for the AHQ adducts (Scheme I) because of the lack of an hydroxyl group in the 10-position of the anthracenyl moiety.

To relate the model reactions to the actual lignin polymer, we found it necessary to prepare AHQ and anthranol adducts with quinone methides generated from lignin. This preparation was recently accomplished[15] with a lignin isolated from loblolly pine (*Pinus taeda*). The spectral and chemical characteristics of the lignin adducts are consistent with those of the corresponding lignin model adducts **3** and **4**.

In the present study the generality of the adduct formation is demonstrated by the reaction of AHQ and anthranol with a variety of lignin model quinone methides. In addition, the results of a detailed NMR examination are presented to lend support for the rather unique stereochemical conformation proposed for the adducts. Investigations concerning formation of these adducts and their subsequent reactions, particularly the degradation pathways (currently under investigation), are in progress and are expected to provide further insight as to the design or selection of more efficient catalysts for wood delignification. Such catalysts should result in more efficient and environmentally sound wood delignification processes that are less demanding on our wood resource.

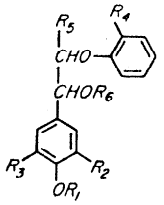
Mechanism of Adduct Formation

Adduct formation is postulated as a nucleophilic attack by AHQ or anthranol on the α-carbon of the quinone methide (Scheme II). Although both the AHQ dianion (AHQ^{-2})[6] and monoanion (AHQ^{-})[11] have been suggested as the nucleophile, we show in this study that AHQ and anthranol also react to give the corresponding adducts in chloroform in the presence of a mild Lewis base (pyridine). Therefore, the ionization state of the nucleophile appears to be relatively unimportant in adduct formation.

The presence of small quantities of anthrasemiquinone (one-electron reduction product of AQ) has been demonstrated in independent ESR studies.[16] Although the possibility of semiquinone involvement cannot be dis-

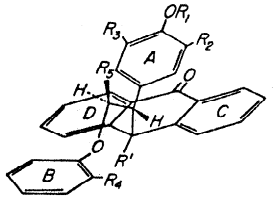
(3) K. Iiyama, A. G. Kulkarni, Y. Nomura, and J. Nakano, *Mokuzai Gakkaishi*, 24 (10), 766 (1978).
(4) B. I. Fleming, G. J. Kubes, J. M. MacLeod, and H. I. Bolker, *Tappi*, 61 (6), 43 (1978).
(5) J. R. Obst, L. L. Landucci, and N. Sanyer, *Tappi*, 62 (1), 55 (1979).
(6) L. L. Landucci, presented at the 1979 Canadian Wood Chemistry Symposium, Harrison Hot Springs, British Columbia, Canada, Sept 19–21, 1979; *Tappi*, 63 (7), 95 (1980).
(7) It is generally accepted that quinone methides are reactive intermediates generated from lignin during alkaline pulping. See ref 8 and 9 for reviews on this subject.
(8) J. Gierer, *Sven. Papperstidn.*, 73 (18), 571 (1970).
(9) J. Marton, "Lignins: Occurrence, Formation, Structure, and Reactions", K. V. Sarkanen and C. H. Ludwig, Eds., Wiley-Interscience, New York, 1971, Chapter 16.
(10) The reduced half of the couple AQ ⇌ AHQ is the active catalyst and is rapidly formed under alkaline pulping conditions by the reaction of AQ with dissolved wood components, as described in ref 5.
(11) (a) J. Gierer, O. Lindeberg, and I. Norēn, *Holzforschung*, 33, 213 (1979). (b) D. R. Dimmel and D. Shepard, *J. Org. Chem.*, 47, 22, 29 (1982).
(12) C. A. Grob and P. W. Schiess, *Angew. Chem. Int. Ed. Engl.* 6 (1), 1 (1967).
(13) T. J. Fullerton, *Sven. Papperstidn.* 78 (6), 224 (1975).
(14) I. Gourang, R. Cassidy, and C. W. Dence, *Tappi*, 62 (7), 43 (1979).
(15) L. L. Landucci, *J. Wood Chem. Technol.*, 1 (1), 61 (1981).
(16) M. B. Hocking, H. I. Bolker, and B. I. Fleming, *Can. J. Chem.*, 58, 1983 (1980).

Table I. Lignin Models



compd	R_1	R_2	R_3	R_4	R_5	R_6
1a	H	OCH_3	H	OCH_3	H	H
b	H	OCH_3	H	H	H	H
c	H	H	H	H	H	H
d	H	OCH_3	OCH_3	OCH_3	H	H
e	H	OCH_3	H	OCH_3	CH_3	H
f	H	OCH_3	H	OCH_3	CH_2OH	H
g	H	OCH_3	H	OCH_3	CH_2OAc	Ac
gAc	Ac	OCH_3	H	OCH_3	CH_2OAc	Ac
h	H	OCH_3	H	OCH_3	CD_2OAc	Ac
hAc	Ac	OCH_3	H	OCH_3	CD_2OAc	Ac
i	CH_2Ph	OCH_3	H	OCH_3	CH_2OH	H
j	CH_2Ph	OCH_3	H	OCH_3	CD_2OH	H
k	CH_2Ph	OCH_3	H	OCH_3	COOEt	H

Table II. Adducts



compd	R_1	R_2	R_3	R_4	R_5
3a, 4a, 6a	H	OCH_3	H	OCH_3	H
3aMe, 4aMe, 5aMe	CH_3	OCH_3	H	OCH_3	H
3aAc, 4aAc, 5aAc	Ac	OCH_3	H	OCH_3	H
3b	H	OCH_3	H	H	H
5bAc	Ac	OCH_3	H	H	H
3c	H	H	H	H	H
3cMe	CH_3	H	H	H	H
5cAc	Ac	H	H	H	H
3d	H	OCH_3	OCH_3	OCH_3	H
3e	H	OCH_3	H	OCH_3	CH_3
3eMe, 4eMe	CH_3	OCH_3	H	OCH_3	CH_3
3eAc, 4eAc	Ac	OCH_3	H	OCH_3	CH_3
3f, 4f	H	OCH_3	H	OCH_3	CH_2OH
3g, 4g	H	OCH_3	H	OCH_3	CH_2OAc
3gAc, 4gAc	Ac	OCH_3	H	OCH_3	CH_2OAc
3hAc, 4hAc	Ac	OCH_3	H	OCH_3	CD_2OAc

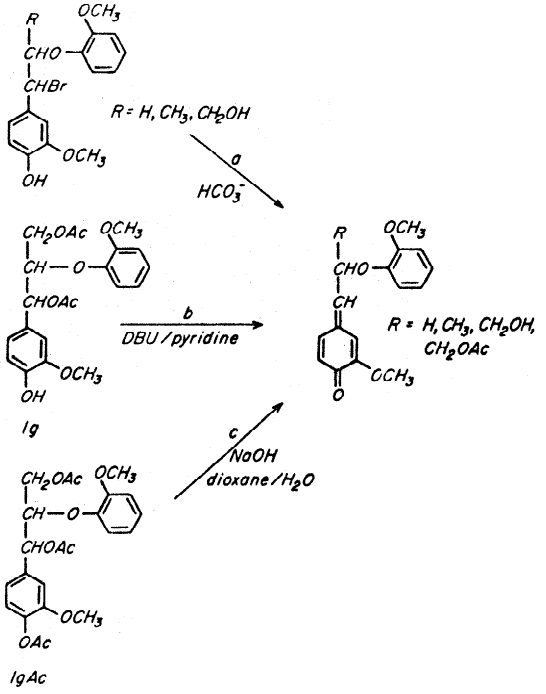
counted, the observation that both AHQ and anthranol (which cannot form a semiquinone) react with quinone methides in an analogous fashion is more consistent with an ionic pathway than a free-radical pathway.

Syntheses of Adducts

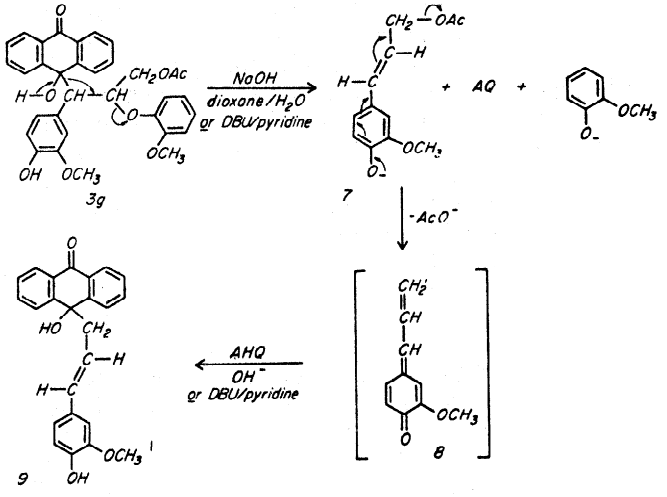
To establish the generality of adduct formation, we used a variety of lignin model quinone methides, all of which contain the important β-aryl ether linkage. Initial studies[6,11] were performed with the guaiacylglycol model 1a, which is one of the most frequently used lignin models because of its relative ease of preparation. However, model 1f (Table I), which has a three-carbon side chain, is a more suitable model since lignin units are almost exclusively of the guaiacylglycerol type.

Quinone methides were readily prepared from the models 1a–f via an α-bromo derivative (method a, Scheme III). The corresponding adducts (Table II) were prepared in high yield (normally >80%) by treating the quinone methides with AHQ or anthrone in the presence of alkali.

Scheme III



Scheme IV



Alternatively (method b, Scheme III), a γ-acetoxymethyl quinone methide was generated in situ by treating the diacetate 1g (prepared by acetylation of 1i followed by debenzylation) with AHQ in pyridine in the presence of a strong nonnucleophilic base such as 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU).[17]

Another in situ method (method c, Scheme III) that is suitable for the γ-acetoxymethyl models involves treatment of the triacetate (1gAc) with AHQ in aqueous dioxane in the presence of a limited amount of alkali such that the aromatic acetate is perferentially hydrolyzed. Then the reaction proceeds as with the diacetates (Scheme III). This latter method has previously been used for the synthesis of adduct 3a[11] and also in the recently successful synthesis of AHQ–lignin and anthranol–lignin adducts.[15]

During the chromatographic purification of adduct 3g it was found to be contaminated with both coniferyl acetate (7) and a novel vinylogous adduct (9, Scheme IV). A possible mechanism to generate 9 is by nucleophilic ad-

(17) On dry days 1,8-bis(dimethylamino)naphthalene gave a significantly cleaner reaction (>80% yield) than DBU but was not as reproducible.

dition to the extended quinone methide 8, derived from the expected fragmentation product 7. The same vinylogous adduct was recently found during the preparation of an AHQ–lignin adduct[15] and was presumably formed from the structure type analogous to that of **3g** in which the β-position is linked to *O*-lignin rather than *O*-(*o*-methoxybenzene).

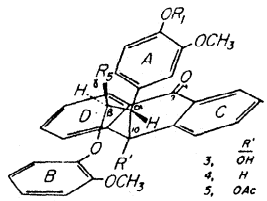
Pronounced instability of AHQ adducts was evident by the appearance of AQ along with unidentified products during synthesis, chromatographic purification attempts, and storage of chloroform solutions. Adducts **3e–h**, derived from guaiacylglycerol models, were particularly sensitive and even decomposed in the solid state. This instability suggests that under neutral conditions a homolytic fragmentation at the C_α–C_{10} bond may be operative.

Interestingly, the aryl propyl adducts (**e–h**, Table II) were all determined to be a single diastereomer that was assigned as "threo"[18] on the basis of their reactions, their ^1H NMR spectra, and their numerous related derivatives.[19]

NMR Spectra

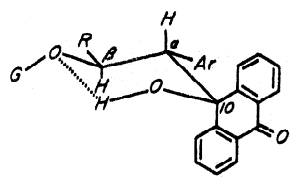
In a previous investigation[6] the conformation of **3a** was postulated on the basis of its rather unique ^1H NMR spectrum. A common feature in the ^1H NMR spectra (Tables III and IV) of the adducts is the presence of a highly shielded methoxyl signal (A3) at about δ 3.4, relative to a typical aromatic methoxyl (for example, B2) that appears at about δ 4.0. In addition, the ring-A protons are also highly shielded, appearing around δ 5.5 (A2 and A6) and 6.4 (A5). These diamagnetic shifts are relatively insensitive to differences in the quinone methide precursor and can be explained by the proximity of these protons within the shielding region of rings C and D. Despite the high shielding of the methoxyl group observed in the ^1H NMR spectra, the shift remains quite invariant in corresponding ^{13}C NMR spectra (Table V).

Calculation of shielding curves[20] indicates that although rotation about the C_{10}–C_α bonds occurs and is fast on the ^1H NMR time scale, ring A is situated symmetrically over the anthracenyl moiety approximately 95% of the time for anthranol **4**, 80–90% for AHQ adducts **3**, and 70% for derivative **5aAc**. Consequently, substitution of larger groups at C_{10} tends to hinder the approach of ring A over the anthracenyl moiety, thus allowing a closer approach (to rings C and D) by ring B. This proximity is indicated by the shielding of the ring B methoxyl in **5aAc** (relative to **3aAc**) and in **6a** (relative to **3a**) as seen in Table III.



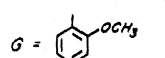
Introduction of γ-carbon in AHQ adducts **3** appears to render the C_{10} position less accessible, as was indicated by the failure to acetylate this position in the γ-methyl adduct **3e** under forcing conditions.[21] Alternatively, a group larger than hydroxyl at C_{10} in combination with a γ-carbon may resutlt in a highly strained molecule. Thus, while an attempt to synthesize an adduct by treating the enolate of 10-methoxyanthrone with an aryl propyl quinone methide (from **1e**) resulted in failure, an analogous treatment with an aryl ethyl quinone methide (from **1a**) resulted in the formation of the expected adduct **6a**.

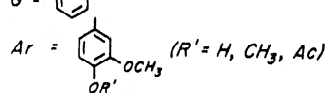
The unusual low field position (δ 6.5) of the aliphatic 10-hydroxyl proton signal in **3a** (R = H) was explained[6] as the result of hydrogen bonding to the guaiacyl oxygen. Infrared spectroscopy at high dilution in CCl_4 supported the conclusion that the hydrogen bonding was intramolecular. Subsequently, it was found that hydrogen



3, "threo" isomer

R = H, CH_3, CH_2OAc

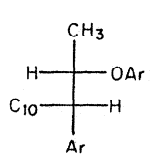




bonding is presumably stronger in AHQ adducts containing a γ-carbon as reflected in the chemical shifts of the 10-hydroxyl protons (**3e–h**, Table IV) compared with the significantly lower range found for the adducts containing no γ-carbon (**3a–d**, Table III). Thus, stronger hydrogen bonding is consistent with a more rigid conformation. Furthermore, the threo isomer can adopt a chairlike conformation consistent with the observed ^1H NMR coupling constants[22] (in particular, $J_{\alpha\beta}$ values in Table IV that indicate an H_α–H_β dihedral angle of approximately 180°). The hydrogen bonding involving the guaiacyl oxygen is relatively temperature independent (–60 to +40 °C) and is obviously a result of the conformation and not the cause of it, since anthranol adducts (no 10-hydroxyl) also adopt this conformation, as indicated by ^1H NMR spectroscopy. In an analogous adduct, **10**, containing no β-guaiacyl moiety, the 10-hydroxy signal has a typical chemical shift (δ 2.7), whereas the diamagnetic shifts of the ring-A substituents still prevail (^1H NMR in Experimental Section).

Hydrogen bonding between the hydroxyl proton and guaiacyl oxygen has been postulated to occur in simple

(18) "Erythro" and "threo" are assigned in analogy with the parent models. Thus, threo is as shown and for **3e** (R = CH_3) is the *RR/SS* isomer. However, "threo" corresponds to the *RS/SR* isomer for the analogous anthranol adduct (**4e**). Consequently, although the *RS* nomenclature is unambiguous, it was avoided as being particularly confusing because of the changing Cahn–Ingold–Prelog priorities (which also vary with the R group).

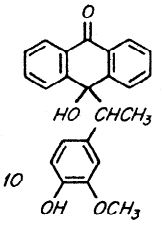


(19) J. Ralph and L. L. Landucci, part 2 of this series.

(20) J. Ralph and L. L. Landucci, unpublished. Approximate shielding curves for the various protons, resulting from rotation of ring A about the C_{10}–C_α axis, have been calculated according to the method of Johnson and Bovey [*J. Chem. Phys.*, 29 (5), 1012 (1958)] for adducts **3** and **4** and for derivatives[19] in which ring A is conformationally "locked" over the anthracenyl moiety. The anthracenyl moiety was assumed to be planar for mathematical simplicity, although it is recognized that the central ring may preferentially adopt a boat conformation, with the large 10-substituent axial to avoid steric interactions with the *peri*-hydrogen atoms at C-1 and C-8.

(21) Although starting material was recovered in the attempted acetylation of **3eAc** in refluxing pyridine/acetic anhydride, the increased lability of the γ-acetoxymethyl adduct (**3g**) resulted in a complex mixture that was not investigated.

(22) Karplus curves were calculated from the empirical equations in C. A. G. Haasnoot, F. A. A. M. DeLeeuw, and C. Altona, *Tetrahedron*, 36, 2783 (1980).



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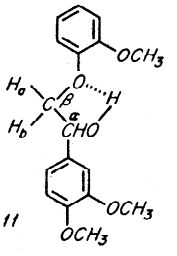
lignin models such as 11.[23] However, the presence of the



11

α-hydroxyl proton signals of such compounds at rather typical values ($\delta \sim 3.5$) suggests that hydrogen bonding is not occurring to any appreciable extent. It was mistakenly assumed by others[23] that such a conformation was necessary to explain the nonequivalence of H_a and H_b (evident from ^1H NMR) via hindered rotation about the C_α–C_β bond, when in fact these methylene protons are diastereotropic and would be expected to be nonequivalent.[24]

In summary, it has been demonstrated that both AHQ and anthranol form analogous adducts with a variety of lignin model quinone methides. Current studies are aimed toward elucidating the alkaline degradation pathways of selected adducts that have features most representative of those found in lignin (for example, **3f** and **4f**, Table II). In addition, AHQ and anthranol adducts of important lignin structural units other than the β-aryl ether type are being synthesized and investigated to obtain a more thorough understanding of the mechanisms involved in the catalytic delignification of wood.

Experimental Section

^1H NMR spectra were determined in $CDCl_3$ or acetone-d_6 on a Varian T-60 or a Bruker WH270 FT spectrometer with Me_4Si as an internal reference (the 270-MHz spectra were run with 16K data points, resulting in J values accurate to ±0.4 Hz). ^{13}C NMR spectra were determined in $CDCl_3$ or acetone-d_6 on a JEOL FX60 or a JEOL FX200 FT spectrometer. Infrared spectra of samples in KBr disks or as films were determined on a Beckman IR-12 spectrometer. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were determined on a calibrated Thomas-Hoover capillary melting point apparatus. Unless otherwise noted all products exhibited only one spot on thin-layer chromatography (silica gel, 10–50% ethyl acetate/hexane as developer). When required, compounds were purified by thick-layer or column chromatography on silica gel. For compounds that were unstable on silica gel (**3e–h**), the sorbent was deactivated by elution with 1% acetic acid in 95% ethanol, followed by equilibration with the required solvent (generally, ethyl acetate–hexane for plates and $CHCl_3/CCl_4$ for columns). Methylations were accomplished with diazomethane in methanol–diethyl ether. Acetylations were performed with 1/1 acetic anhydride–pyridine [often containing a trace of 4-(dimethylamino)pyridine]. All adduct preparations and related operations were done under a nitrogen atmosphere, and reagent solutions and solvents were purged with nitrogen prior to use.

Preparation of Starting Materials. Lignin Models. All parent models in Table I except **1c** and **1g** were synthesized according to literature procedures.[25–29] Compound **1c** was synthesized by a modified procedure[30] in which a benzoyl rather than a benzyl protecting group was incorporated. Compound **1g** was prepared by acetylating **1i**, followed by debenzylation in the usual fashion,[27] giving a quantitative yield of an oil composed of erythro and threo isomers.[31] The deuterated models (**1h**, **1hAc**, and **1j**) were prepared via the ester **1k**[26] with lithium aluminum deuteride.

Quinone Methides. The most frequently used method (a, Scheme III) is a modification of literature procedures.[32,33] Hydrogen bromide was passed through a solution or suspension of the lignin model (10–500 mg) in methylene chloride or chloroform (10–50 mL) for 10 min at room temperature. The resulting solution was cautiously shaken with an equal volume of saturated bicarbonate until a bright yellow color due to the quinone methide appeared. The solution was shaken an additional 30–60 s, and then the organic layer was separated, treated with anhydrous $MgSO_4$, filtered, and immediately cooled in a dry ice/2-propanol bath until used. Alternatively, the in situ methods (b and c, Scheme III) were used in some instances and are detailed under the appropriate preparations.

Anthrahydroquinone (AHQ and AHQ^{2-}). Typically, for preparation of an alkaline solution of the red dianion AHQ^{2-}, a mixture of AQ (0.50 g, 2.4 mmol), sodium dithionite (0.60 g, 3.4 mmol), and 1 M NaOH (50 mL) was stirred under nitrogen at 40 °C for approximately 1 h, or until no significant amount of undissolved solid remained. In most cases this solution was used directly since the excess dithionite did not interfere with subsequent steps. Alternatively, neutral AHQ was precipited as a yellow solid by adding either hydrochloric or acetic acid. The aqueous fraction was removed and the precipitate washed two or three times with deaerated water to remove salts. The AHQ was then either dissolved in alkali or dried by heating under a stream of nitrogen followed by dissolution in $CHCl_3$/pyridine or pyridine.

Anthranol. A solution of the anion of anthranol was prepared by refluxing a mixture of anthrone (0.5 g) and 1 M NaOH (50 mL) under nitrogen until dissolution was complete (~1 h).

Adducts. General Procedure. Most of the adducts (Table II) could be prepared by the following method that is a modification of one previously reported[6] for the synthesis of **3a**. The cold quinone methide solution (1 mmol) was added over a 5–10-min period to the vigorously stirred aqueous AHQ^{2-} (or $anthranol^{1-}$) solution (0.9 mmol) through an open neck of a three-necked reaction flask fitted with a nitrogen inlet. Nitrogen flow was continued throughout the addition during which a temperature of 45 °C (35 °C for **3e**) was maintained. Following the addition, the alkaline mixture was extracted with $CHCl_3$. The extract was dried over $MgSO_4$ and evaporated, leaving the adduct as an oil or amorphous solid (>80% except for **3f**).

1-(3-Methoxy-4-acetoxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)ethane (3aAc). Room-temperature acetylation of **3a** gave **3aAc** in quantitative yield as a pale yellow oil: IR (neat) $\nu_{C=O}$ 1680 (vs), 1768 (s) cm^{-1}. Crystallization from $CHCl_3$/petroleum ether gave white crystals: mp 165.6–166.5 °C (slow heating), 125–127 °C (fast heating). The white solid obtained on cooling the melt had a melting point of 165.5–166.5 °C.

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(31) The isomeric ratio is dependent upon the method of preparation of **1i** but is not important in this study as stereochemistry is lost upon subsequent quinone methide formation.
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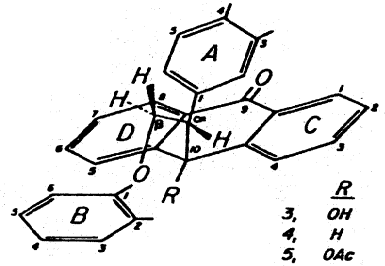
(34) The side chain protons in **5aAc** were misassigned in ref 11. Also, the same misassignment was made in ref 6 for the 4-OCH_3 (ring A) analogue (**5aMe**, Table II) on the basis of a 60-MHz spectrum.

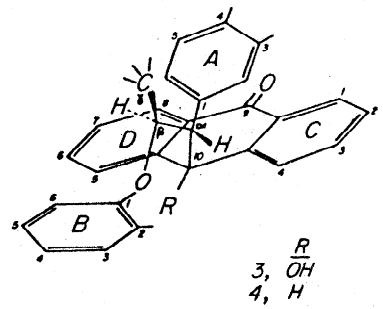
Table III. ^{1}H NMR Data for Adducts with Aryl Ethyl Lignin Models[a,e]



compd	freq, MHz	solvent[b]	methoxyls A3	methoxyls A4	methoxyls B2	ring A 2	ring A 5	ring A 6	ring A 4-OH	$J_{5,6}$	$J_{6,2}$	ring B	rings C and D 2-7	rings C and D 1,8[d]	10-H	10-OH	α	β_1	β_2	$J_{10\text{-}\alpha}$	$J_{\alpha\beta_1}$	$J_{\alpha\beta_2}$	$J_{\beta_1\beta_2}$	acetate methyl
3a[6]	270	C	3.42		4.02	5.43 (d)	6.43 (d)	5.55 (dd)	5.45	8.1	1.8	6.88–7.07 (m)	7.36–7.86 (m)	8.05–8.09 (dd, dd)		6.53	3.60 (t)	4.23 (d)				7.2		
3a	270	C + D	3.37		3.81	5.52 (d)	6.35 (d)	5.5 (c)	5.49	8.1	1.8	6.89–6.97 (m)	7.34–7.91 (m)	7.99–8.16 (dd, d)		6.47	3.57 (dd)	4.18 (dd)	4.57 (dd)		7.0	7.4	9.6	
3aMe[6]	270	A	3.33	3.63	3.76	5.64 (c)	6.40 (d)	5.65 (dd)		8.1	2.2	6.80–7.01 (m)	7.38–7.80 (m)	7.92–8.17 (c, dd)		6.06	3.62 (dd)	4.24 (dd)	4.67 (dd)		7.4	6.6	9.6	
3aMe	270	C	3.37	3.70	3.93	5.48 (d)	6.34 (d)	5.55 (dd)		8.3	1.8	6.82–7.04 (m)	7.28–7.81 (m)	8.01–8.12 (dd, d)		6.45	3.60 (dd)	4.18 (dd)	4.27 (dd)		4.8	9.6	9.7	
3aAc	270	C	3.35		3.99	5.61 (d)	6.56 (d)	5.67 (dd)		8.1	1.8	6.82–7.08 (m)	7.32–7.88 (m)	8.05–8.16 (dd, dd)		6.49	3.60 (dd)	4.24 (bd)			7.4	6.3		2.22
4a	270	C	3.38		3.97	5.4 (c)	6.42 (d)	5.54 (dd)	5.4 (c)	8.1	1.8	6.96–7.05 (m)	7.33–7.61 (m)	7.95–8.08 (d, dd)	5.14 (d)		3.61 (ddd)	4.15 (dd)	4.29 (dd)	3.7	4.4	10.7	10.3	
4aMe	270	C	3.37	3.73	3.96	5.48 (d)	6.37 (d)	5.57 (dd)		8.1	1.8	6.92–7.08 (m)	7.33–7.63 (m)	7.95–8.09 (d, dd)	5.15 (d)		3.62 (ddd)	4.15 (dd)	4.30 (dd)	4.0	4.8	10.3	9.9	
4aAc	60	C	3.33		3.95	5.59 (bs)	6.55 (d)	5.65 (c)		9	2	6.80–7.10 (m)	7.30–7.66 (m)	7.85–8.20 (m)	5.13 (d)		3.4–4.4 (m)			4	?	?	?	2.20
5aAc[34]	270	C	3.37		3.65	5.85 (d)	6.62 (d)	5.91 (dd)		8.1	1.5	6.71–6.94 (m)	7.35–7.64 (m)	8.00–8.21 (dd, dd)			3.86 (dd)	4.11 (dd)	4.62 (dd)		8.1	4.8	9.4	2.22
6a	270	A	3.33		3.56	5.64 (d)	6.28 (d)	5.59 (dd)	?	8.1	2.2	6.82–6.97 (m)	7.46–8.01 (m, c)	7.97–8.13 (dd, dd)	3.12 (10-CH_3)		3.67 (dd)	4.21 (dd)	5.00 (dd)		10.3	3.3	9.2	
3b	60	C	3.38			5.5 (c)	6.43 (d)	5.58 (c)	5.5 (c)	8	2	6.75–8.15 (m)				5.0	3.3–4.7 (m)				?	?	?	
5bAc	270	C	3.39			5.86 (bs)	6.71 (d)	5.98 (bd)		8.1	?	6.64–6.95 (m, c)	7.20–7.68 (m)	8.05–8.22 (d, d)			3.77 (dd)	4.06 (dd)	4.55 (dd)		7.9	4.8	9.7	2.23, 2.24
3c	60	C				5.82 (bd)	6.38 (bd)	5.82 (bd)	5.2	9	?	6.8–8.2 (m)				5.2	3.4–4.6 (m)				?	?	?	
3cMe	60	C		3.67		5.97 (m)	6.42 (bd)	5.97 (m)		9	?	6.7–8.1 (m)				5.0	3.4–4.6 (m)				?	?	?	
5cAc	270	C				6.35 (bd)	6.73 (d)	6.35 (bd)		8.6	<1	6.66–7.67 (m)		8.04–8.21 (dd, dd)			3.81 (dd)	4.04 (dd)	4.51 (dd)		8.5	4.8	9.6	2.21, 2.22
3d	60	C	3.43		4.02	5.23		5.23	5.35			6.85–7.05 (m)	7.30–8.15 (m)			6.40	3.4–4.3 (m)				?	?	?	

[a] Chemical shifts are in δ units and coupling constants in hertz. [b] C = $CDCl_3$, A = acetone-d_6, and D = Me_2SO-d_6. [c] Overlapping other protons. [d] $J_{1,2}$ and $J_{8,7} \simeq 7.5$–8.1 Hz; $J_{1,3}$ and $J_{8,6} \simeq 0.7$–1.5 Hz. [e] Abbreviations: d = doublet, dd = doublet of doublets, bd = broad doublet, bs = broad singlet, m = multiplet, t = triplet.

Table IV. ^{1}H NMR Data for Adducts with Aryl Propyl Lignin Models[a]



3, R = OH
4, R = H

compd	freq, MHz	solvent[b]	methoxyls A3	methoxyls A4	methoxyls B2	ring A 2	ring A 5	ring A 6	ring A 4-OH	$J_{5,6}$	$J_{6,2}$	ring B	rings C and D 2-7	rings C and D 1, 8[e]
3e	60	C	3.43		4.02	5.37 (c)	6.37 (d)	?	5.5	8	?	—6.7-8.2 (m)—		
3eMe	270	A	3.36	3.64	4.02	5.60 (bs)	6.39 (d)	5.57 (c)		8.1	?	6.98-7.22 (m)	7.34-7.78 (m)	8.01-8.28 (dd, dd)
3eAc	270	C	3.37		4.01	5.55 (bs)	6.52 (d)	5.55 (bs)		8.1	?	6.88-7.07 (m)	7.25-7.82 (m)	8.07-8.27 (dd, d)
4eMe	270	C	3.33	3.72	4.01	5.30 (d)	6.34 (d)	5.44 (bd)		8.5	1.8	7.01-7.12 (m)	7.26-7.79 (m)	8.02-8.05 (dd, dd)
4eAc	270	C	3.28		3.99	5.39	6.51 (d)	5.46 (bd)		8.1	?	6.98-7.09 (m)	7.32-7.78 (m)	7.92-8.04 (dd, d)
3f	270	A	3.39		4.02	5.6 (c)	6.28 (d)	5.52 (bd)	5.62	8.1	?	6.92-8.28 (m)		
4f	270	C	3.34		3.97	5.32 (bs)	6.39 (d)	5.42 (bd)	5.52	8.1	~1	7.03-7.16 (m)	7.32-7.79 (m)	7.89-8.07 (m)
3g[d]	270	C	3.43		4.02	?	6.38 (d)	?	?	8.1	?	—6.9-8.1 (m)—		
3gAc	270	C	3.37		4.04	5.58 (c)	6.54 (bd)	5.59 (c)		7.7	?	6.96-7.12 (m)	7.32-7.83 (m)	8.09-8.29 (dd, d)
3gAc	270	A	3.39		3.98	5.87 (d)	6.54 (d)	5.79 (dd)		8.1	1.8	6.92-7.18 (m)	7.36-7.78 (m)	8.04-8.27 (dd, d)
4g[d]	270	C	3.34		4.01	5.24 (d)	6.38 (d)	5.4 (c)	?	8.1	1.5	6.9-8.1 (m)		
4gAc	270	C	3.28		4.00	5.40 (d)	6.52 (d)	5.49 (bd)		8.1	1.8	6.90-7.10 (m)	7.23-7.80 (m)	7.92-8.03 (d, dd)
4gAc	270	A	3.28		4.04	5.60 (c)	6.51 (d)	5.59 (d, c)		8.5	1.8	7.00-7.19 (m)	7.37-8.01 (m)	
3hAc	270	A	3.40		3.99	5.87 (d)	6.54 (d)	5.79 (dd)		8.1	1.8	6.93-7.20 (m)	7.35-7.91 (m)	8.04-8.28 (dd, dd)
4hAc	270	C	3.28		4.00	5.40 (d)	6.52 (d)	5.48 (dd)		8.1	1.8	7.00-7.12 (m)	7.34-7.80 (m)	7.93-8.03 (dd, dd)
4hAc	270	A	3.28		4.04	5.60 (c)	6.51 (d)	5.59 (dd, c)		8.8	2.2	7.04-7.19 (m)	7.37-8.01 (m)	

[a] Chemical shifts are given in δ units and coupling constants in hertz. Table III, footnote *e*, for abbreviations (also ddd = was a mixture of **3g** and **4g**, but all the values tabulated were assigned with reasonable certainty. [e] $J_{1,2}$ and $J_{8,7}$ ≃ 7.5-8.1

***threo*-1-(3-Methoxy-4-acetoxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propane (3eAc).** Neutral AHQ (1.09 g, 5.19 mmol) prepared as above was suspended in deaerated $CHCl_3$ (50 mL). Pyridine (15 mL) was then added, causing the AHQ to dissolve. A $CHCl_3$ solution of the quinone methide prepared from **1e** (1.51 g, 4.97 mmol) was added over a 10-min period at room temperature. The solution was then washed several times with 5% sulfuric acid, followed by saturated bicarbonate. The organic layer was dried over $MgSO_4$ and evaporated, leaving a yellow glassy solid (2.33 g, 95%). Purification

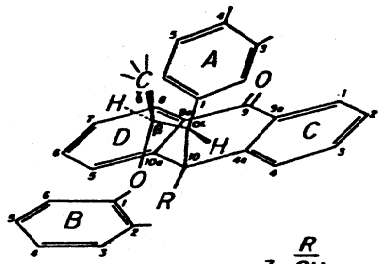
10-H	10-OH	α	β	γ_1	γ_2	$J_{10\text{-}\alpha}$	$J_{\alpha\beta}$	$J_{\beta\gamma_1}$	$J_{\beta\gamma_2}$	$J_{\gamma_1\gamma_2}$	misc
	f	~3.5 (c)	4.65 (dq)	1.05 (d)			10	6			
	f	3.51 (d)	4.83 (dq)	1.03 (d)			10.3	5.9			
	7.1	3.52 (d)	4.69 (dq)	1.07 (d)			10.3	5.9			
5.37 (d)		3.42 (dd)	4.77 (dq)	1.07 (d)		3.3	10.7	5.9			
5.38 (d)		3.46 (dd)	4.79 (dq)	1.10 (d)		3.3	10.7	5.9			2.20 (OAc)
	f	3.90 (d)	4.73 (bd)	3.13 (m)	?		10.3	?	?	?	
5.26 (d)		3.81 (dd)	4.56 (ddd)	3.13 (ddd)	3.60 (ddd)	2.9	11.0	1.8	2.6	12.5	2.62 (dd, J = 9.9, 3.3 Hz, γ-OH
	6.87	3.71 (d)	4.81 (ddd)	3.75–3.85 (m)			10.3	?	?	12.5	1.82 (OAc)
	6.87	3.73 (d)	4.84 (ddd)	3.82 (dd)	4.10 (dd)		10.3	3.7	4.0	12.5	1.79, 2.22 (OAc)
	6.77	3.87 (d)	5.05 (ddd)	3.73 (dd)	4.29 (dd)		9.9	3.3	2.9	12.5	1.82, 2.14 (OAc)
5.26 (d)		3.55 (dd)	4.94 (ddd)	3.89 (dd)	4.10 (dd)	2.9	11.0	5.2	2.6	12.5	1.82 (OAc)
5.30 (d)		3.60 (dd)	4.99 (ddd)	3.98 (dd, *c*)	4.13 (dd)	2.9	11.0	4.8	3.3	12.1	1.79, 2.20 (OAc)
5.36 (d)		3.76 (dd)	5.20 (ddd)	3.85 (dd)	4.17 (dd)	2.9	11.0	4.4	2.9	12.5	1.81, 2.13 (OAc)
	6.75	3.88 (d)	5.04 (d)				10.3				1.83, 2.14 (OAc)
5.30 (d)		3.60 (dd)	4.99 (d)			2.9	11.0				1.78, 2.20 (OAc)
5.35 (d)		3.76 (dd)	5.19 (d)			2.9	11.0				1.81, 2.13 (OAc)

doublet of doublets, dq = doublet of quartets). [b] C = $CDCl_3$; A = acetone-d_6. [c] Overlapping other protons. [d] The NMR Hz, and $J_{1,3}$ and $J_{8,6} \simeq 0.7$–1.5 Hz. [f] Probably hidden under aromatic protons.

on a deactivated silica gel column (70% $CHCl_3/CCl_4$) gave an 80% yield of **3eAc**. Also eluted from the column was AQ and about 10% of a 1/1 mixture of guaiacol acetate and isoeugenol acetate, fragmentation products of **3eAc**. Crystallization of **3eAc** from methylene chloride/hexane gave pale yellow crystals: mp 205–205.5 °C; IR (KBr) $\nu_{C=O}$ 1673 (s), 1769 (s) cm^{-1}; ^1H NMR, Table III; ^{13}C NMR, Table V. Anal. Calcd for $C_{33}H_{30}O_7$ (mol wt 538.60): C, 73.59; H, 5.61. Found: C, 73.28; H, 5.60.

***threo*-1-(3-Methoxy-4-hydroxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propan-3-ol (3f).**

Table V. ^{13}C NMR Data for Adducts[a]



	R
3,	OH
4,	H
6,	OCH_3

				chemical shift											
											aromatic carbons				
compd	freq, MHz	solvent[b]	methoxyls	C-9	C-10	C-α	C-β	C-γ	acetate methyls	acetate carbonyls	A2,5; B3,6	A6; B4,5	A1; C1-4, 9a; D5-8a	A3,4; B2; C4a; D10a	B1
3a	15	C	55.6, 55.9	182.9	*c*	59.0	70.9				111.8–113.8	120.9–122.5	126.0–134.0	143.4–147.3	149.5
3a	15	A	55.8, 56.4	182.3	76.6	60.3	71.0				111.8–113.4	120.9–122.4	125.8–128.0	143.4–148.5	149.4
3aMe	15	C	55.5, 55.9, 55.9	182.3	75.0	58.9	70.7				110.5–113.4	120.8–122.4	125.8–134.0	143.3–148.6	149.4
3aMe	15	A	55.6, 56.1, 56.4	182.4	76.6	60.3	70.9				112.0–115.2	121.8–122.7	126.1–133.5	145.0–149.5	150.7
4a	15	C	55.6, 56.1	183.6	44.4	55.0	69.6				111.9–115.3	121.1–122.1	126.4–134.6	140.7–148.1	150.3
6a	50	C	55.5, 56.2 (52.7)[d]	181.8	81.9	59.8	69.4				112.4–115.2	121.0–122.7	126.3–134.4	140.5–148.8	150.1
3eMe	50	A	55.6, 55.9, 56.2	182.1	77.1	66.4	77.7	19.5			112.0–114.5[g]	121.5–122.6[h]	125.7–133.5	144.4–149.2	150.4
3eAc	15	C	55.5, 55.9	182.1	*e*	66.3	*e*	19.4	20.5	168.4	111.9–113.7[g]	121.0–122.2[h]	126.1–135.0	139.1–149.8	150.3
4eAc	15	A	55.6, 56.5	183.2	44.3	64.4	74.3	18.9	20.3	168.3	113.8–117.3[g]	121.8–122.7[h]	126.6–135.4	139.8–151.8[f]	150.8[f]
3gAc	15	A	55.7, 56.4	182.6	77.2	62.5	78.4	64.1	20.3	168.4. 170.3	113.2–115.6[g]	121.6–123.5[h]	126.3–135.0	140.0–150.8[f]	151.0[f]
4f	50	C	55.6, 56.1	183.2	43.6	56.9	80.9	60.8			112.5–113.7[g]	118.3–123.3[h]	125.6–135.0	141.0–146.4	151.2

[a] Chemical shifts are given in δ units. [b] C = $CDCl_3$, A = acetone-d_6. [c] Resonance masked by $CDCl_3$ peaks, values of δ 182.6 (C-9) and 77.2 (C-10) were for the 9,10-^{13}C-labeled adduct. [d] C-10 methoxyl. [e] Masked by $CDCl_3$ peaks. [f] Peaks interchangeable within interpretation. [g] For A2,5 and B3 only. [h] For A6 and B4–6.

Compound **3f** was prepared according to general procedure except that a temperature of 0 °C was maintained. Due to the instability of this adduct only a low yield was obtained, and purification was not feasible.

***threo*-1-(3-Methoxy-4-hydroxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)-3-acetoxypropane (3g).** AHQ (135 mg, 0.65 mmol) was prepared and dried as described above and was dissolved in pyridine (15 mL). A solution of the free phenol diacetate **1g** (137 mg, 0.33 mmol) in pyridine (5 mL) was added followed by dropwise addition of DBU[17] (49 mg, 0.32 mmol) in pyridine (2 mL) at room temperature. The bright red color, characteristic of ionized AHQ, was discharged after 20 min at 40 °C at which time the solution was extracted with $CHCl_3$. The extract was washed with 5% HCl and saturated bicarbonate, dried over $MgSO_4$, and evaporated, leaving a residue that was immediately acetylated in pyridine/acetic anhydride. The crude product (225 mg) upon column chromatography gave three products in addition to unreacted starting material and AQ: **3gAc** (32 mg, 0.054 mmol, 16%), an unidentified polymeric substance (47 mg, 21%), and the diacetate of 9 [*trans*-1-(3-methoxy-4-hydroxyphenyl)-3-(10-hydroxy-9-oxoanthracen-10-yl)propene] (19 mg, 8%); NMR, IR, and mass spectral data have been described previously.[15]

***threo*-1-(3-Methoxy-4-hydroxyphenyl)-1-(9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propan-3-ol (4f).** This compound was prepared according to the general procedure: 90% yield% white crystals from CH_2Cl_2/cyclohexane; mp 135–140 °C (with gas evolution); from ethyl acetate/hexane, mp 149–155 °C (rapid heating), 201–204 °C (slow heating), gas evolution. In addition to the data in Table IV, the γ-OH group is a very clear double doublet (dd) coupled to each γ-proton; $J_{OH\text{-}\gamma_1}$ = 9.9 Hz, $J_{OH\text{-}\gamma_2}$ = 3.31 Hz. The γ-protons each appear as ddd's that collapse to dd's upon addition of D_2O. Anal. Calcd for $C_{31}H_{28}O_6$ (mol wt 496.56): C, 74.98; H, 5.68. Found: C, 74.97; H, 5.82. IR (film) ν_{OH} 3520 (sharp), 3420 (br), $\nu_{C=O}$ 1665 cm^{-1}.

***threo*-1-(3-Methoxy-4-hydroxyphenyl)-1-(9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)-3-acetoxypropane (4g).** A mixture of anthrone (46 mg, 0.23 mmol) and NaOH solution (5 mL containing 0.47 mmol of NaOH) was refluxed for 35 min. Deaerated dioxane (2 mL) was added, and the orange solution was cooled to room temperature after which a solution of triacetate **1gAc** (110 mg, 0.25 mmol) in dioxane (2 mL) was added. The solution was stirred overnight at room temperature and then worked up as in the general procedure, giving a crude product (150 mg). Chromatogaphy (column, followed by thick-layer) on deactivated silica gel gave pure **4g** as a pale yellow oil: 86 mg (0.61 mmol, 70%); ^1H NMR, Table IV. Diacetate (**4gAc**, also obtained by acetylating **4f**): IR (neat) $\nu_{C=O}$ 1768 (s), 1745 (vs), 1670 (s) cm^{-1}; ^1H NMR, Table IV.

1-(3-Methoxy-4-acetoxyphenyl)-1-(10-acetoxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)ethane (5aAc)[11]. Acetylation of **3a** with 1/1 Pyr/Ac_2O at reflux temperature gave **5aAc** as a colorless oil: IR (neat) $\nu_{C=O}$ 1670 (s), 1764 (vs) cm^{-1}.

1-(3-Methoxy-4-hydroxyphenyl)-1-(10-methoxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)ethane (6a). This compound was prepared by allowing the quinone methide of **1a** to react with 10-methoxyanthrone according to the general procedure, followed by thick-layer chromatography (50% yield). Crystallization from acetone gave pale yellow crystals: mp 175.5–179.5 °C; IR (film) $\nu_{C=O}$ 1670, ν_{OH} 3390 cm^{-1}. Anal. Calcd for $C_{31}H_{28}O_6$ (mol wt 496.56): C, 74.98; H, 5.68. Found: C, 74.75; H, 5.80.

1-(3-Methoxy-4-hydroxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)ethane (10). Obtained by the general procedure from 1-(3-methoxy-4-hydroxyphenyl)ethanol and AHQ^{2-} as a pale yellow oil: 95% yield; ^1H NMR (60 MHz, $CDCl_3$) δ 1.10 (d, methyl, $J_{\beta\alpha}$ = 7.5 Hz), 2.70 (s, C_{10} OH), 3.13 (q, H_α, $J_{\alpha\beta}$ = 7.5 Hz), 3.48 (s, methoxyl), 5.44 (s, phenolic proton), 5.68 (d, H_2, ring A, $J_{2,6}$ = 1.5 hz), 5.88 (dd, ring A, $J_{6,5}$ = 8 Hz, $J_{6,2}$ = 1.5 Hz), 6.53 (d, H_5, ring A, $J_{5,6}$ = 8 Hz), 7.2–8.1 (m, anthrone ring protons).

Acknowledgment. We are very grateful to Lester Zank and Martin Wesolowski for the excellent ^1H NMR (60 MHz) and IR service, to John R. Obst for valuable discussions, to Professor Raymond A. Young (Department of Forestry, University of Wisconsin, Madison) for continuing support, and to members of the New Zealand Research Advisory Council for their partial funding of this project.

Registry No. **1a**, 7382-68-5; **1b**, 82246-93-3; **1c**, 82246-94-4; **1d**, 18167-89-0; **1e**, 1774-10-3; **1f**, 7382-59-4; **1g**, 82246-95-5; **1gAc**, 22317-32-4; **1h**, 82246-96-6; **1hAc**, 82246-97-7; **1i**, 22400-03-9; **1j**, 82246-98-8; **1k**, 82246-99-9; **3a**, 74838-64-5; **3aMe**, 74838-65-6; **3aAc**, 82247-00-5; **3b**, 82247-01-6; **3c**, 82247-02-7; **3cMe**, 82247-03-8; **3d**, 82247-04-9; **3e**, 82247-05-0; **3eMe**, 82247-06-1; **3eAc**, 82247-07-2; **3f**, 82247-08-3; **3fAc**, 82247-09-4; **3g**, 82247-10-7; **3gAc**, 82247-11-8; **3hAc**, 82247-12-9; **4a**, 82247-13-0; **4aMe**, 74838-66-7; **4aAc**, 82247-14-1; **4eMe**, 82247-15-2; **4eAc**, 82247-16-3; **4f**, 82247-17-4; **4g**, 82247-18-5; **4gAc**, 82247-19-6; **4hAc**, 82247-20-9; **5aMe**, 74838-67-8; **5aAc**, 82247-21-0; **5bAc**, 82247-22-1; **5cAc**, 82247-23-2; **6a**, 82247-24-3; **10**, 79769-76-9; 9,10-anthracenediol, 4981-66-2; 9-anthracenol, 529-86-2; 10-methoxyanthrone, 14629-83-5; lignin, 9005-53-2; anthraquinone, 84-65-1.